

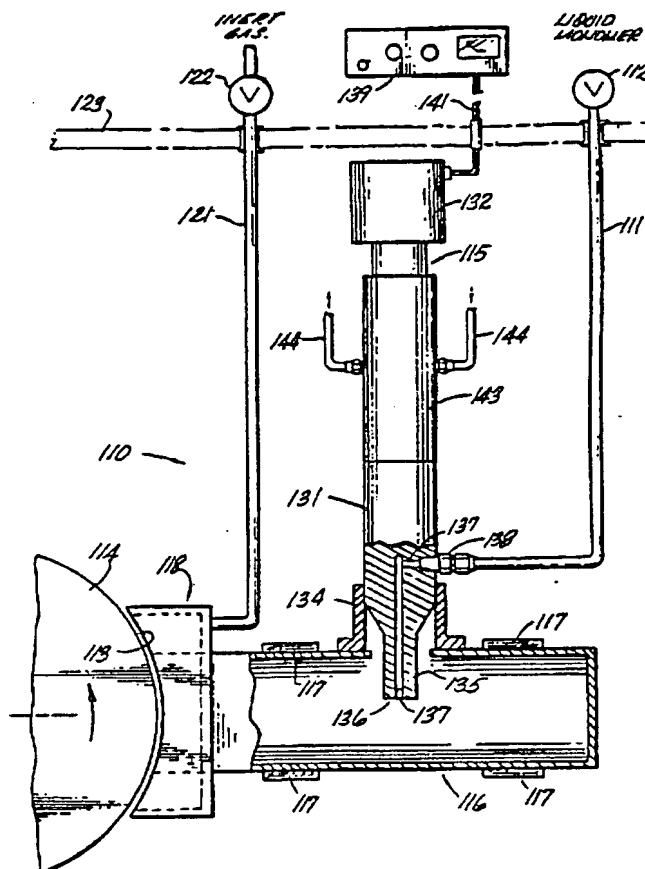


INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

| | | |
|--|-----------|--|
| (51) International Patent Classification 4 : B01D 1/16, B05D 1/02, 5/12 C23C 16/00 | A1 | (11) International Publication Number: WO 87/ 07848 (43) International Publication Date: 30 December 1987 (30.12.87) |
| (21) International Application Number: PCT/US87/01455 (22) International Filing Date: 23 June 1987 (23.06.87) (31) Priority Application Number: 877,175 (32) Priority Date: 23 June 1986 (23.06.86) (33) Priority Country: US (71) Applicant: SPECTRUM CONTROL, INC. [US/US]; 2185 West Eighth Street, Erie, PA 16505 (US). (72) Inventor: YIALIZIS, Angelo ; 9095 North Oracle Road, No. 1205, Tucson, AZ 85704 (US). (74) Agent: DALY, Thomas, J.; Christie, Parker & Hale, P.O. Box 7068, Pasadena, CA 91109-7068 (US). | | (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i> |

(54) Title: FLASH EVAPORATION OF MONOMER FLUIDS**(57) Abstract**

A method for continuously supplying a uniform vapor of a polymerizable and/or cross-linkable material. A continuous liquid flow of said material is supplied at a temperature below both the decomposition temperature and the polymerization temperature of said material and atomized into a continuous flow of liquid droplets having a particle size from about 1 to about 50 microns. The droplets are continuously vaporized upon contact with a heated surface which is maintained at a temperature at or above the boiling point for said material, but below the temperature at which said droplets would undergo pyrolysis before vaporizing. The vapor may be deposited onto a substrate and subsequently polymerized or cross-linked.



1

5

-1-

10

FLASH EVAPORATION OF MONOMER FLUIDS

Field of the Invention

The present invention relates to a method for depositing a liquid film on a substrate and, more particularly, to a method for depositing a monomeric film on a substrate. Such a film may be polymerized or cross-linked to form a polymeric layer on said substrate.

Cross-References

20

25

30

35

This invention is related to the following copending, commonly assigned, U.S. patent applications and patents: Serial No. 620,647, filed June 14, 1984, entitled "Miniaturized Monolithic Multi-layer Capacitor and Apparatus and Method for Making"; Patent No. 4,499,520, issued February 12, 1985, entitled "Capacitor with Dielectric Comprising Poly-Functional Acrylate Polymer and Method of Making"; Patent No. 4,490,774, issued December 25, 1984, entitled "Capacitors Containing Polyfunctional Acrylate Polymers as Dielectrics"; Patent No. 4,533,710, issued August 6, 1985, entitled "1,2-Alkanediol Diacrylate Monomers and Polymers Thereof Useful as Capacitor Dielectrics"; Patent No. 4,513,349, issued April 23, 1985, entitled "Acrylate-Containing Mixed Ester Monomers and Polymers Thereof Useful as Capacitor Dielectrics"; Patent No. 4,515,931, issued May 7, 1985, entitled "Polyfunctional

1 Acrylate Monomers and Polymers Thereof Useful as Capacitor
Dielectrics"; Patent No. 4,586,111, issued April 29, 1986,
entitled "Capacitor with Dielectric Comprising a Polymer of
Polyacrylate Polyether Pre-Polymer"; Serial No. 668,918,
5 filed November 6, 1984, entitled "Atomizing Device for
Evaporation"; and Serial No. 692,746, filed January 18,
1985, entitled "Monomer Atomizer for Evaporator"; all of
which are hereby incorporated by reference.

10 Background and Objects of the Invention

Various industries require the ability to place thin
coatings of polymeric materials onto selected substrates.
One such industry is the electronics industry, especially
the portion thereof which is concerned with the manufacture
15 of polymer monolithic capacitors. Other industries which
rely on the production of thin polymeric coatings on
various substrates include magnetic tape manufacturers and
producers of packaging films.

Capacitors are used in a wide variety of electrical
circuits, for example, in relatively high voltage AC power
20 systems (such as the common 110-volt systems) and in
relatively low voltage (e.g., under 50 volts) DC systems
frequently encountered in printed circuits and the like.
Important factors which must be considered in the
manufacture of such capacitors are volumetric efficiency,
25 temperature of operation, dissipation factor, especially in
AC systems, and behavior upon failure.

The development of electronic devices and circuits of
reduced size has led to a need for significantly smaller
capacitors having increased volumetric efficiency, or
30 capacitance per unit volume. The polymer-monolithic
capacitor has been used for such applications.

A monolithic capacitor is one in which the layers of
electrodes and dielectric are bonded together in a unitary
structure as opposed, for example, to a metallized film
35

1 capacitor in which self-supporting films are rolled or
wound into the capacitor form. A miniaturized capacitor is
one of very small dimensions, so as to be suitable for
microcircuitry. Small overall size could denote low
5 capacitance of little practical value, except that the
thickness of the intervening dielectric layer inversely
affects the capacitance between adjacent electrodes, and
the number of electrode pairs and dielectric constant of
the dielectric directly affects capacitance. Therefore, as
10 a matter of basic capacitor theory, a capacitor having very
thin dielectric layers, and many pairs of electrodes or a
given capacitor with a dielectric having a high dielectric
constant could have substantial capacitance despite being
of miniature size with the active area of the electrodes
being quite small.

15 One such type of polymer monolithic multi-layer
capacitor is described in application Serial No. 620,647,
cross- referenced herein. That capacitor has a
capacitively active section, and two electrode joining
20 sections, each separated from the active section by a
sloping section. The capacitor includes a first and second
set of electrode layers interleaved with one another, each
layer of each set having an active area extending through
and contributing to the capacitively active section of the
25 capacitor in a stacked and spaced apart relationship with
the active areas of all of the other layers. The electrode
layers are joined at the margin in stacked electrically
contacting relationship and each layer has a sloped portion
between its active area and its margin which contributes to
30 a sloped section of the capacitor. A dielectric coating is
in contact with and between each adjacent electrode pair.
The dielectric coating has a substantially uniform
thickness in the capacitively active section and tapers to
zero thickness through the sloping section.

35 The volumetric efficiency of a capacitor, including

1 the monolithic multi-layer capacitor described above, is
normally measured in terms of capacitance per unit volume.
Generally, high efficiency is desirable, with values of at
least about one-tenth (0.1) microfarad per cubic millimeter
5 for a 50 VDC rated unit being preferred.

As noted above, the volumetric efficiency of the
capacitor may be increased by reducing the thickness of the
dielectric layer and/or by increasing the number of
electrode pairs, both of which may have limits depending
10 upon the capacitor type and its end use.

From the foregoing, it is evident that in order to
achieve the results which are desired in accordance with
the aforementioned application Serial No. 620,647, a method
for depositing a thin uniform monomeric layer on the
desired substrate is absolutely essential. Heretofore, it
15 has been known generally in the art that monomeric layers
may be deposited upon substrates. For example, U.S. Patent
No. 3,547,683 and the British counterpart thereof, No.
1,168,641 deal with the vapor deposition of a polymerizable
or cross-linkable material which has a vapor pressure under
20 standard temperature and pressure conditions of less than 1
Torr. It appears that the concept embodied in such patents
is simply to allow a heated container of the material to
vaporize the desired polymerizable or cross-linkable
material. Such an approach suffers from the fact that by
25 maintaining a polymerizable or cross-linkable material at
an elevated temperature for any substantial length of time
gives rise to the possibility of degradation and/or
polymerization of the material, within the container, both
of which are undesirable.

30 U.S. Patent Nos. 4,121,537 and 4,207,836 are both
concerned with the vapor deposition of a layer of a
compound consisting of two or more kinds of elements such
as Se, Te or As through flash evaporation, as by dropping
raw material, bit-by-bit, into a boat heated to a high
35

1 temperature with the individual bits being vaporized within
a short time. Thus, the approach of using flash
evaporation is not taught in said patents to relate to
monomeric materials as used in the present invention. A
5 problem with such an approach, as taught in said patents,
of course, is that as each drop is vaporized, a burst of
vapor is produced, followed by an intermittent period of
time during which no vapor is present. Under such
conditions, it is difficult to achieve a uniform layer of
10 material on the desired substrate. The foregoing is
especially true if the source of the vapor and the
substrate are moving in relation to each other.

U.S. Patent No. 4,153,925 is concerned with the use of
electron bombardment or ultraviolet radiation of an organic
monomer to make a dielectric layer, generally. However,
15 there is no specific teaching regarding the method by which
the monomer is placed on the desired substrate. Likewise,
U.S. Patent Nos. 4,277,516; 4,301,765 and 4,378,382 deal
with the glow polymerization of monomers, without any
specific indication of how one might achieve a desired
20 uniform monomeric layer. It is believed that the monomers
which are glow polymerized and to which those patents
relate, are monomers which are typically present under
standard temperature and pressure conditions as a gas and
thus do not present the same problem as do monomers which
25 are typically used as liquids.

Thus, especially in view of the process disclosed in
the aforementioned application, Serial No. 620,647, there
exists a need for a method by which polymerizable and/or
cross-linkable materials may be uniformly deposited upon a
30 desired substrate in a controlled manner such that said
materials may be subsequently cured to form a desired
polymeric layer on said substrate. More generally, a need
exists for a method by which materials may be quickly and
uniformly deposited upon a desired substrate.
35

1

Summary of the Invention

5

10

15

Generally, the present invention provides a method for depositing onto a substrate a layer of material, which may be a polymerizable and/or cross-linkable material, said material being characterized by the fact that it is chemically unstable at or below its boiling point, said method comprising vaporizing said material by continuously placing droplets of said material into contact with a heated surface which is maintained at a temperature at or above the boiling point for said material, but below the temperature at which said droplets would undergo pyrolysis before vaporizing; maintaining at least a portion of said substrate at a temperature which is below the boiling point of said material and in a region which is at a lower pressure than said vaporized material, to provide a positive flow of vaporized material toward said substrate; and directing the flow of vaporized material onto said substrate in a predetermined manner.

20

25

30

In accordance with the present invention, there is also provided a method for continuously supplying a uniform vapor of a material, which may be a polymerizable and/or cross-linkable material, said method comprising supplying a continuous liquid flow of said material at a temperature below both the decomposition temperature and the polymerization temperature of said material, continuously atomizing the liquid flow into a continuous flow of airborne liquid droplets having a particle size from about 1 to about 50 microns, and continuously vaporizing said liquid droplets by causing said droplets to contact a heated surface which is maintained at a temperature at or above the boiling point for said material, but below the temperature at which said droplets would undergo pyrolysis before vaporizing.

35

The present invention thus also provides a method for

-7-

1 depositing a layer of a material, which may be a
polymerizable and/or cross-linkable material, on a
substrate comprising supplying a continuous liquid flow of
5 said material at a temperature below both the decomposition
and the polymerization temperature, if any, of said
material; continuously atomizing said liquid flow into a
continuous flow of liquid droplets having a particle size
from about 1 to about 50 microns; continuously vaporizing
10 said liquid droplets by causing said droplets to contact a
heated surface which is maintained at a temperature at or
above the boiling point for said material but below the
temperature at which said droplets would undergo pyrolysis
before vaporizing; maintaining at least a portion of said
15 substrate at a temperature which is below the boiling point
of said material and in a region which is at a lower
pressure than said vaporized material, to provide a
positive flow of vaporized material toward said substrate;
and directing the flow of vaporized material onto said
substrate in a predetermined manner.

20 From the foregoing, it should also be apparent that
when the material is polymerizable and/or cross-linkable,
by employing the additional step of polymerizing or cross-
linking the material on said substrate, a method is also
provided for depositing a polymeric coating on at least a
25 portion of the desired substrate.

30

35

1 Brief Description of the Drawings

 Fig. 1 is a schematic perspective of an apparatus useful in the practice of the method of the present invention;

5 Fig. 2 is an enlarged fragmentary section of a portion of the apparatus shown in Fig. 2 illustrating the operating phenomenon created;

 Fig. 3 is a top view, with a portion sectioned, of the structure shown in Fig. 2;

10 Fig. 4 is similar to Fig. 3 but illustrates the droplet dispersion resulting from operation of the apparatus;

 Fig. 5 is a schematic partially sectioned apparatus embodying an atomizer useful in performing the process in accordance with the invention; and

15 Fig. 6 is a schematic of an apparatus used to manufacture polymer monolithic capacitors, employing the method of the present invention.

20

25

30

35

1 Detailed Description of the Preferred Embodiments

As discussed, the present invention provides a method for depositing a uniform film of a polymerizable and/or cross-linkable material onto a substrate. The polymerizable and/or cross-linkable material may be referred to hereinafter as a monomer or monomeric material. However, as will be detailed below, the material may itself be polymeric in nature.

Thus, the monomers which are useful in the present invention include all such materials disclosed in the cross-referenced applications discussed above, which are hereby specifically incorporated by reference.

In addition, other monomeric materials which are useful in the practice of the present invention include those discussed in U.S. Patent No. 3,547,683, including, but not limited to, low molecular weight addition-type polymers, natural oils, silicone, condensation polymers, and other monomers and materials containing unsaturation which are capable of undergoing polymerization or cross-linking.

From the viewpoint of operability in the present process, any monomer employed herein should either be a liquid at room temperature or should be capable of being converted to a liquid at an elevated temperature, without undergoing any significant decomposition or polymerization. Furthermore, the monomeric materials should have a vapor pressure at standard temperature and pressure, of less than about 1 Torr and preferably less than about 10^{-3} Torr. It is also contemplated that monomers useful in the present invention include those monomers which, although not themselves a liquid at room temperature are capable of being dissolved in other suitable liquids to form an azeotropic solution.

The particularly preferred monomeric materials for use in the present invention are the polyacrylate polyether

-10-

1 prepolymers disclosed in the cross-referenced U.S. Patent
No. 4,586,111, issued April 29, 1986.

5 The monomers used in the present invention are
generally characterized by the fact that they are
chemically unstable at temperatures at or even below their
boiling point. The term "chemically unstable" is used
herein to refer to any type of chemical instability,
including, but not limited to, oxidation or other chemical
degradation of the monomer as well as the formation of
10 polymers or oligomers.

As indicated above, the first step in the method of
the present invention involves continuously supplying
droplets of the monomer. Such droplets may be produced by
continuously supplying a stream of the liquid monomer and
continuously atomizing said monomer into a continuous flow
15 of droplets which preferably are uniform liquid droplets
having a particle size from about 1 to about 50 microns.
Typically, the particle size of the liquid droplets will be
from about 1 to about 20 microns and most typically will be
centered around particles having a particle size from about
20 5 to about 10 microns.

Although, in general, the atomized droplets employed
in the present process will fall within the size range of
about 1 to about 50 microns, it is theoretically best to
25 use the smallest particle size possible. Thus, particles
of less than 1 micron in size may be advantageously
employed in the present invention. However, from a
practical viewpoint, it is not usually possible to atomize
the monomers into such a fine particle size, so other
30 considerations must be used to determine the largest
particle size which will be acceptable.

It is, of course, to be appreciated that when
discussing the largest particle size employed in any given
embodiment of the present invention, the actual droplets
employed will have a particle size distribution range
35

1 peaking at some level significantly below the maximum
particle size. Thus, for example, in a typical embodiment
of the present invention the particle size employed may
range from about 1 to about 20 microns, with the
5 distribution peak occurring at about 10 microns. As used
herein, it is to be appreciated that the "particle size" of
a particle is meant to refer to the diameter of that
particle.

10 It should be understood that a principal goal of the
present invention is to achieve vaporization of the monomer
particles from the heated surface in such a manner that no
fluid accumulates on said substrate. Thus, to achieve a
continuous flow of monomer vapor by vaporizing monomer
15 droplets from the heated surface, the size of those monomer
droplets typically needs to be such that the vaporization
of the monomer deposited from each droplet will occur in
less than about 50 milliseconds, more typically within less
than about 20 milliseconds, and most typically within less
than about 10 milliseconds. Ideally, it would be preferred
20 for the vaporization of the monomer to occur in less than 1
millisecond. However, practical limitations again usually
dictate that the vaporization occur in the range from about
10 to about 20 milliseconds. The actual length of time
needed for vaporization is, of course, dependent upon many
25 considerations, besides the size of the monomer droplet.
Such considerations include the nature of the monomer, such
as its vapor pressure under standard temperature and
pressure conditions, the degree of vacuum under which the
heated surface is placed, and the temperature to which the
30 surface is heated.

35 The exact mechanism for atomizing said liquid monomer,
in general, is not critical and any suitable method may be
employed. However, for many applications it is critical
that the method of atomizing said liquid monomer be precise
in that substantially all of the particles fall within the

1 desired size range and that the particles are supplied in a
continuous flow which is thus not intermittent in nature.
The need for the continuous flow is evident when
5 considering the fact that the typical ultimate use may be
the deposition of a uniform polymer layer as, for example,
a dielectric coating in a monolithic capacitor structure.

One suitable method for atomizing the liquid monomer
is disclosed in the cross-referenced application Serial No.
668,918 and another such method is disclosed in Serial No.
10 692,746, filed January 18, 1985, entitled "Monomer Atomizer
for Evaporation".

Employing the apparatus taught in either of the two
aforementioned applications in the manner described therein
will result in the generation of monomer particles of the
15 desired size range, in a continuously flowing, uniform
stream. Any other device may be employed to atomize the
liquid monomer, so long as it results in the generation of
the desired size of particles in a uniform, continuous
flow.

20 With respect to the step of vaporizing the liquid
droplets, again, any suitable heated surface may be
employed. The temperature of the heated surface should be
such that vaporization occurs instantaneously upon contact
with the surface by the monomer droplets. However, the
25 temperature should also not be so high as to cause
pyrolysis of the material, that is to cause oxidation or
other degradation of the monomer structure itself.

With respect to the physical form of the heated
surface, any desirable shape may be employed. Various
30 structures are shown in the cross-referenced applications.
It is usually desirable for the heated surface to be
contained in or to actually form a vaporization chamber in
which the liquid droplets may be vaporized. Such a chamber
may also define a means for directing the flow of monomer
35 vapor onto a substrate. In such an embodiment, the chamber

1 may terminate in the form of a flow directing means, or
nozzle, such that the liquid monomer droplets upon being
vaporized create an internal pressure within the chamber
causing the monomer vapor to be expelled out the nozzle or
5 other flow directing means in the direction of the
substrate.

In the manufacture of monolithic capacitors, the
preferred substrate is a copper sheet. As may be
appreciated, in the manufacture of monolithic capacitors,
10 the copper sheet may itself be coated with layers of
polymeric material, alternating with layers of conducting
material, such as aluminum about 200 to 500 angstroms
thick. Thus, a typical substrate would be a copper sheet
on which alternating layers of polymeric material formed
15 through the method of the present invention and alternating
conducting layers of aluminum are present.

The substrate itself should be located in a region
which is maintained at a lower pressure than the pressure
generated through the vaporization of the monomer droplets.
20 With respect to the pressure employed as in the manufacture
of monolithic capacitors, the pressure in the deposition
zone is usually below 10 Torr, preferably below 10^{-1} Torr
and advantageously 10^{-4} Torr, or even less.

The layer of film of monomeric material deposited on
25 the substrate may be any suitable depth. However, the
depth of the deposited film should usually be such that the
subsequent means of polymerization or cross-linking will be
effective in curing the monomeric material throughout
substantially its entire depth.

30 With respect to the step of polymerizing the deposited
film, any suitable methods may be employed. Thus, thermal,
electron beam, or ultraviolet radiation curing may be
employed, depending upon the nature of the monomer. A
particularly suitable method for curing employs the use of
35 a beam of accelerated electrons whose energy is generally

1 up to about 20 kev, as are available from conventional
electron accelerators. The energy of the irradiation and
the length of time for which the monomeric film is exposed
to the radiation should be such as to polymerize or cross-
5 link the material throughout its thickness. The present
invention, in its preferred embodiments, may be further
appreciated by reference to the drawings and the following
description.

Two different apparatus have been developed for flash
10 vaporizing a liquid according to the present invention.
These apparatus will now be described in detail. It is to
be understood, however, that these apparatus are not the
only apparatus which can be used in practicing the present
invention. Any apparatus capable of continuously atomizing
15 a liquid to the appropriate particle size and continuously
vaporizing the liquid particles in contact with a heated
surface could be used to advantage in the present
invention.

Turning to Fig. 1, there is shown a first embodiment
20 of an apparatus 10 for vaporizing a liquid, such as a
monomeric resin, supplied in a reservoir 11 and depositing
by condensing the resulting vapor on a substrate 12
arranged to move past the apparatus 10. It will be
understood that both the apparatus 10 and the substrate 11
25 are maintained in a low vacuum environment. The intent of
the vapor deposition is to deposit a uniform, very thin--
one micron or less -- coating of the liquid material on the
substrate 12.

The apparatus includes a vaporization chamber 13
30 formed with a nozzle opening 14 for emitting the vaporized
material in close proximity to the substrate 12. The
chamber 13 encloses a spinning disk 15 driven by a motor 15
which throws by centrifugal force atomized droplets of
fluid against a band heater 17 defining a heating surface
18 surrounding the disk 15. The tiny droplets are flash
35

1 vaporized upon contact with the heated surface 18, thereby
developing both vapor and vapor pressure to expel the
gaseous material through the nozzle opening 14 for
condensation on the substrate 12. When the fluid is a
5 monomeric liquid, the flash vaporization preserves the
chemical structure, and the condensed monomer film on the
substrate can be later cured, if desired, by any suitable
technique such as applying ultraviolet or electron beam
radiation.

10 In accordance with the invention, the atomizing device
includes, in addition to the driven disk 15, a capillary
tube 20 mounted on the reservoir 11 for delivering fluid at
right angles to the flat circular face 21 of the disk 15,
and the end of the tube 20 is spaced from the face 21 so
15 that a liquid drop formed at the tube end is just contacted
by the face. With the proper spacing, disk face speed and
drop size, the face rotates the drop as shown in Fig. 2
while pulling a fluid film on the face 21 free from the
drop, which fluid film is continuously replenished from the
20 tube 20, and the film is thrown centrifugally in atomized
droplets having a particle size from about 1 to about 20
microns, from the periphery of the disk onto the heated
vaporizing surface 18. The droplets will be thrown from
the disk surface 21 along the path lines 22 illustrated in
Fig. 4.

25 If the tube 20 is initially positioned near the center
of the spinning disk 15 and then moved peripherally outward
so as to gradually increase the speed of the surface
contacting the drop, the condition described above and
illustrated in Fig. 2 will be reached. Representative
30 relationships found suitable for a monomeric liquid resin
included a 20 mil capillary tube feeding liquid to a disk
1" in diameter driven in the 3,000 to 5,000 rpm range. The
formed drop, depending upon the liquid's viscosity and
surface tension, contacted the disk with the tube end
35

-16-

1 spaced about 37 mils from the disk. The disk was formed of
clean glass. The drop rolling and film forming phenomenon
was achieved with the spacing 23 (see Fig. 3) of the drop
from the disk center being about $3/8$ ". Droplets are
5 produced and discharged along the paths 22.

While the disk surface 21 has been illustrated as
horizontal with the tube at a vertical right angle, the
surface 21 can be disposed vertically and the tube
horizontal so long as the tube is positioned so that the
10 drop contacts the upwardly driven half of the disk surface.
So disposed, the viscosity pull of the disk on the liquid
counteracts the gravity pull.

The arrangement described produces a continuous rate
of very low volume droplets well suited for subsequent
15 flash vaporization and deposition of a very thin coating
layer. The vapor delivery rate can be increased, if
desired, by pressurizing the reservoir 11. Liquids of
varying viscosity would produce initial droplets of varying
size depending upon the size of the capillary tube, but
20 the disk and tube relative spacing could obviously be
readily varied to accommodate varying drop sizes.

Fig. 5 is a schematic partially sectioned apparatus
embodying a second, and presently preferred, embodiment of
an atomizer useful in performing the process in accordance
25 with the invention.

Turning to Fig. 5, there is shown another apparatus
110 for vaporizing a monomeric liquid supplied through a
line 111 and valve 112, and vacuum depositing the vapor
onto a surface 113 carried by a rotating drum 114. The
liquid is atomized by a structure 115 embodying the
30 invention, vaporized in a vaporization chamber 116 heated
by heaters 117, and deposited through nozzle structure 118
onto the drum surface 113. The nozzle structure 118
controls the vapor deposition in part by confining vapor
flow with inert gas, supplied through a line 121 and valve
35

1 122. The apparatus 110 is mounted within a vacuum chamber
123.

5 In accordance with this second and preferred
embodiment, the structure 115 is essentially integrally
formed with a tip portion 131 at one end extending, and
delivering liquid, into the vaporization chamber 116 and
having an ultrasonic vibration device 132 coupled at the
10 opposite end. The structure 115 is supported by a collar
134 that closes the chamber opening through which the tip
portion 131 extends and which is fixed to the tip portion
at approximately its nodal point. The tip portion 131 has
a necked-down tip 135 ending in a surface 136 to which the
liquid is directed through a capillary passage 137 in the
tip portion 131 that is connected to the liquid feed line
15 11 by a compression coupling 138. The device 132,
preferably a piezoelectric crystal transducer, is energized
by an electronic power supply 139 through a line 141.
Ultrasonic vibration of the tip 135 and its surface 136
causes the liquid to flow from the passage 137, coat the
20 surface 136 and be dispersed in fine droplets through a
widespread pattern in the chamber 116. The pattern seen is
in the form of a shallow cone when a substantially flat
surface like the surface 136 is utilized. Upon striking
the hot chamber walls, temperatures of 350° to 400°F being
25 typical, the liquid is vaporized, creating gaseous pressure
driving the vapor through the nozzle structure 118 so as to
be deposited on the surface 113.

The lengths of the coupling 143 and tip portion 131
correspond to one-half wavelength of the vibration, and the
30 device 132 is operated at their fundamental frequency mode
with maximum amplitude of motion at the surface 136 and
minimum movement, or node positions, at the attachment
points of the coupling 143 and tip portion 131. To protect
the vibration device 132 from heat, the structure 115
includes a cooling coupling 143 interposed between and
35

1 rigidly connected to the tip portion 131 and the vibration
device 132. Cooling water is directed through a passage in
the coupling 143 using lines 144. The coupling 143 and the
cooling water absorb and remove heat conducted from the
5 vaporization chamber 116 along the tip portion 131 so that
extreme temperatures cannot adversely affect the vibrating
device 132. To minimize vibration absorption, the lines
138, 144 and the connection with the collar 134 are located
at or near the vibration node positions. The structure 115
10 is left supported cantilever fashion by the collar 134 so
that the device 132 can vibrate undampened.

It has been found that a material like titanium alloy
6AL4V is suitable for the tip portion 131. The diameter of
the passage 137 is dependent upon the flow rate of the
15 liquid being conveyed through the line 111, and diameters
of 20 mils to 1/8" have been found suitable.

The basic structure represented by the tip portion
131, vibration device 132 and electronics 139 can be found
in standard laboratory equipment such as ultrasonic
emulsifying devices and this utilization of relatively
20 standard components makes the atomizer structure economical
to manufacture and maintain.

Capacitors made using the method of the present
invention may be formed of materials and in configurations
known in the art. The conductive materials are typically
25 aluminum, zinc, alloys of these metals and bi-layers
involving at least aluminum or zinc and another metal, with
aluminum being preferred. Aluminum and zinc are unique
because of their contribution to the self healing
properties of a capacitor. For example, one embodiment of
30 the present invention provides a capacitor which includes a
first electrode which may be, for example, an aluminum
layer, a dielectric coating of a polymer formed by
deposition of a monomeric material in solution, on the
surface of the first electrode by the method of the present
35

1 invention, followed by polymerization and a second
electrode which is a second thin metallized layer
preferably of aluminum deposited on the dielectric film.
Suitable leads are attached to the first and second
5 electrodes.

The present invention likewise is useful in the
manufacture of polymer monolithic multi-layer capacitors
such as those described and claimed in application Serial
No. 620,647. Capacitors of this type may be produced by
10 depositing alternating electrode and dielectric layers so
as to provide alternate electrode layers with portions
projecting from the stack and contacting each other in
electrically connected relation as more fully described in
that application. The dielectric coating comprises a
15 polymer which is formed by using the method of the present
invention to deposit a layer of a monomeric material on the
electrode and subsequent polymerization of the monomeric
material. The use of electron beam polymerization is
particularly preferred because it provides rapid
20 polymerization of the pre-polymer without the need for
additional curing agents, and thus leads to economical
production of very thin coatings.

The method of the present invention wherein the layer
of monomeric material is deposited on a substrate and
subsequently polymerized or cross-linked may thus be
25 employed in the manufacture of polymer monolithic
capacitors using an apparatus arranged as shown in Fig. 6
which includes apparatus arranged within and around a
chamber 230 which is either a vacuum chamber or a housing
divided into vacuum portions. Within a vacuum environment
30 is a carrier 231, a dielectric deposit system 232, a
monomer curing system 233, and an electrode material
deposit system 234. A substantial vacuum is required down
to the order of 1×10^{-4} Torr.

35 The carrier 231 is a water cooled drum 235 driven by a

1 motor 236 and whose outer cylindrical surface 237 defines a
rapidly moving continuous surface passing through a
dielectric forming zone and an electrode forming zone. The
regions in which the drum surface 237 and the systems 232,
5 233 are located constitute the dielectric forming zone, and
the region in which the drum surface 237 and the system 234
are located constitute an electrode forming zone. Drum
rotation creates the machine direction 226, which is the
direction the surface passes through the dielectric forming
10 zone and the electrode forming zone.

Because of the small dimensions involved, the surface
237 should be smooth and true. The sheet of substrate 213
is firmly secured to the drum 35 and, when in place, the
outer surface of the substrate defines the surface 237.
15 The drum 235 is cooled to about 70°F so as to facilitate
condensation of the vapor deposits, and the apparatus
functions at drum surface speeds of 150 to 600 feet per
minute.

The electrode material deposit system 234 includes a
conventional electron beam vaporization device 241 such as
20 those used for metallizing film within a vacuum
environment. The rate of vaporization is sensed by a
conventional quartz monitoring device 242 providing
feedback for controlling the rate at which aluminum is
vaporized by the device 241.
25

The alternate pattern of metal vapor deposition is
obtained by shifting the mask 243 axially of the drum 235
upon each drum revolution. A mask motor 247 makes the
shifting movement through a simple mechanical connection
248. A controller 250 is connected to the drum motor 236
30 for sensing drum revolution, and the controller 250
supplies the appropriate shifting signal to the mask
shifting motor 247. It is desirable to keep the mask 243
close to the surface onto which the metal vapor is being
deposited, and this closeness is maintained by a mask
35

1 retraction motor 251 which steps the mask away from the surface 237 upon each drum revolution, as signalled by the controller 250, through a distance approximating the thickness of the electrode layer being deposited.

5 As it is convenient to energize the device 241 and bring it into stable operating condition before beginning to make capacitors, a removable shutter 252 is interposed between the device 241 and the mast 243 for closing off the passage of vapor until the shutter 252 is withdrawn.

10 As a feature of the invention, the dielectric deposit system 232 flash vaporizes the dielectric in monomer form as discussed above in conjunction with Figs. 1 through 5.

15 The condensed liquid monomer is radiation cured by the second system 233 in the dielectric forming zone which includes a radiation source, preferably a gas discharge electron beam gun.

20 The overall operation of the apparatus of Fig. 6 can now be readily understood. Electrode layers are deposited, coated with dielectric and the dielectric cured, before the surface on which the electrode layers are deposited passes again for successive electrode layers and dielectric coatings. Desired thicknesses of the electrode layers and dielectric coatings are determined by matching the rate of vapor deposition with the surface speed of the drum 235.

25 The above description has paid particular attention to application of the method of the present invention in making polymer monolithic multi-layer capacitors. However, the method of the present invention should not be understood as being limited to such an application or even limited to depositing a monomeric film on a substrate for subsequent polymerization and/or cross-linking. The method of the present invention can be used to advantage in any application requiring a controlled supply of vaporized material. For example, if the material to be evaporated is a mixture of components having different vapor pressure,

30

35

1 flash vaporization provides a supply of vapor wherein the
components are present in the same ratios as in the
mixture. This would not be true of a supply of vapor
created by bulk evaporation of the mixture. Thus, flash
5 vaporization is particularly beneficial in any application
requiring a controlled supply of a vaporized mixture, such
as chemical vapor deposition.

10

15

20

25

30

35

-23-

1 WHAT IS CLAIMED IS:

1. A method for continuously supplying a uniform vapor of a material, said method comprising:

5 supplying a continuous liquid flow of said material at a temperature below both the decomposition temperature and the polymerization temperature, if any, of said material;

continuously atomizing the liquid flow into a continuous flow of liquid droplets having a particle size from about 1 to about 50 microns; and

10 continuously vaporizing said liquid droplets by causing said droplets to contact a heated surface which is maintained at a temperature at or above the boiling point for said material, but below the temperature at which said droplets would undergo pyrolysis before vaporizing.

15 2. The method of claim 1 wherein the liquid droplets have a particle size from about 1 to about 20 microns.

20 3. A method for depositing onto a substrate a layer of material, said material being characterized by the fact that it is chemically unstable at or below its boiling point, said method comprising:

25 vaporizing said material by continuously placing droplets of said material into contact with a heated surface which is maintained at a temperature at or above the boiling point for said material, but below the temperature at which said droplets would undergo pyrolysis before vaporizing;

30 maintaining at least a portion of said substrate at a temperature which is below the boiling point of said material and in a region which is at a lower pressure than said vaporized material, to provide a positive flow of vaporized material toward said substrate; and

35 directing the flow of vaporized material onto said substrate in a predetermined manner.

SUBSTITUTE SHEET

1

4. The method of claim 3 wherein the liquid droplets have a particle size from about 1 to about 20 microns.

5

5. The method of claim 3 wherein the substrate is maintained in a region which is at a pressure below about 10^{-1} Torr.

10

6. The method of claim 3 wherein the material is polymerizable and/or cross-linkable and also comprising the step of polymerizing or cross-linking the material on said substrate.

15

7. The method of claim 6 wherein the material is polymerized and/or cross-linked throughout its thickness by use of electron beam curing.

20

8. A method for depositing a layer of a material on a substrate comprising:

supplying a continuous liquid flow of said material at a temperature below both the decomposition and the polymerization temperature, if any, of said material;

25

continuously atomizing said liquid flow into a continuous flow of liquid droplets having a particle size from about 1 to about 50 microns;

30

continuously vaporizing said liquid droplets by causing said droplets to contact a heated surface which is maintained at a temperature at or above the boiling point for said material but below the temperature at which said droplets would undergo pyrolysis before vaporizing;

35

maintaining at least a portion of said substrate at a temperature which is below the boiling point of said material and in a region which is at a lower pressure than said vaporized material, to provide a positive flow of vaporized material toward said substrate; and

1 directing the flow of vaporized material onto said
substrate in a predetermined manner.

5 9. The method of claim 8 wherein the liquid droplets
have a particle size from about 1 to about 20 microns.

10 10. The method of claim 8 wherein the substrate is
maintained in a region which is at a pressure below about
 10^{-1} Torr.

10 11. The method of claim 8 wherein the material is
polymerizable and/or cross-linkable and also comprising the
step of polymerizing or cross-linking the material on said
substrate.

15 12. The method of claim 11 wherein the material is
polymerized and/or cross-linked throughout its thickness by
use of electron beam curing.

20

25

30

35

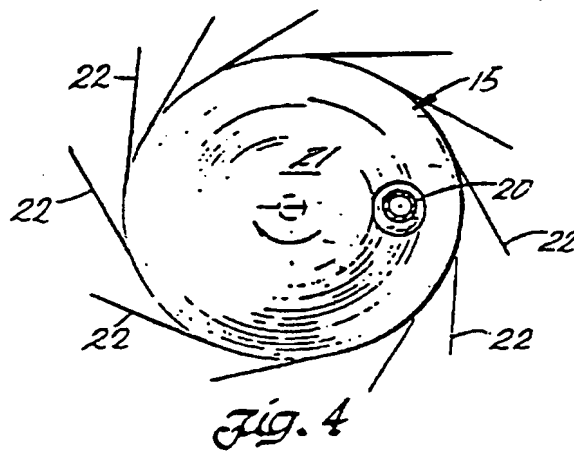
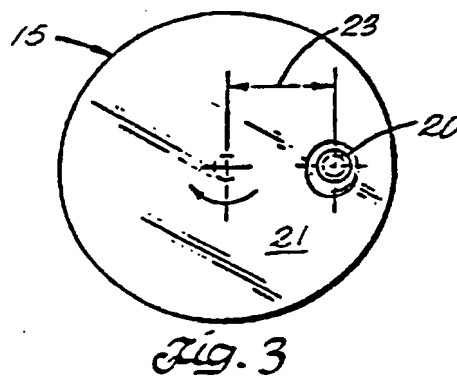
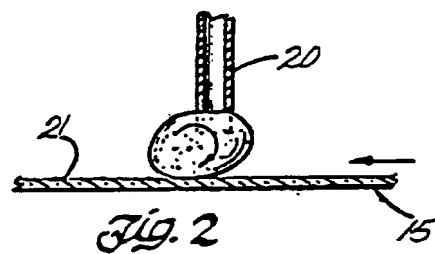
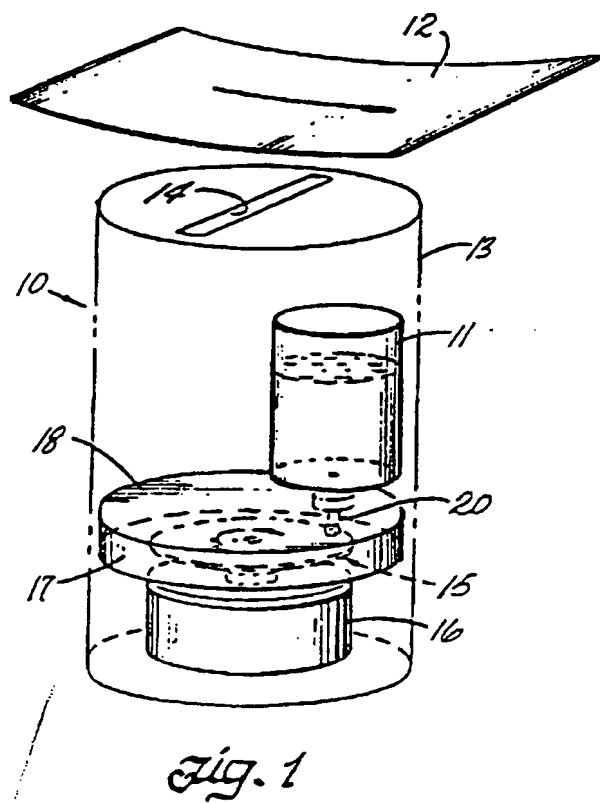
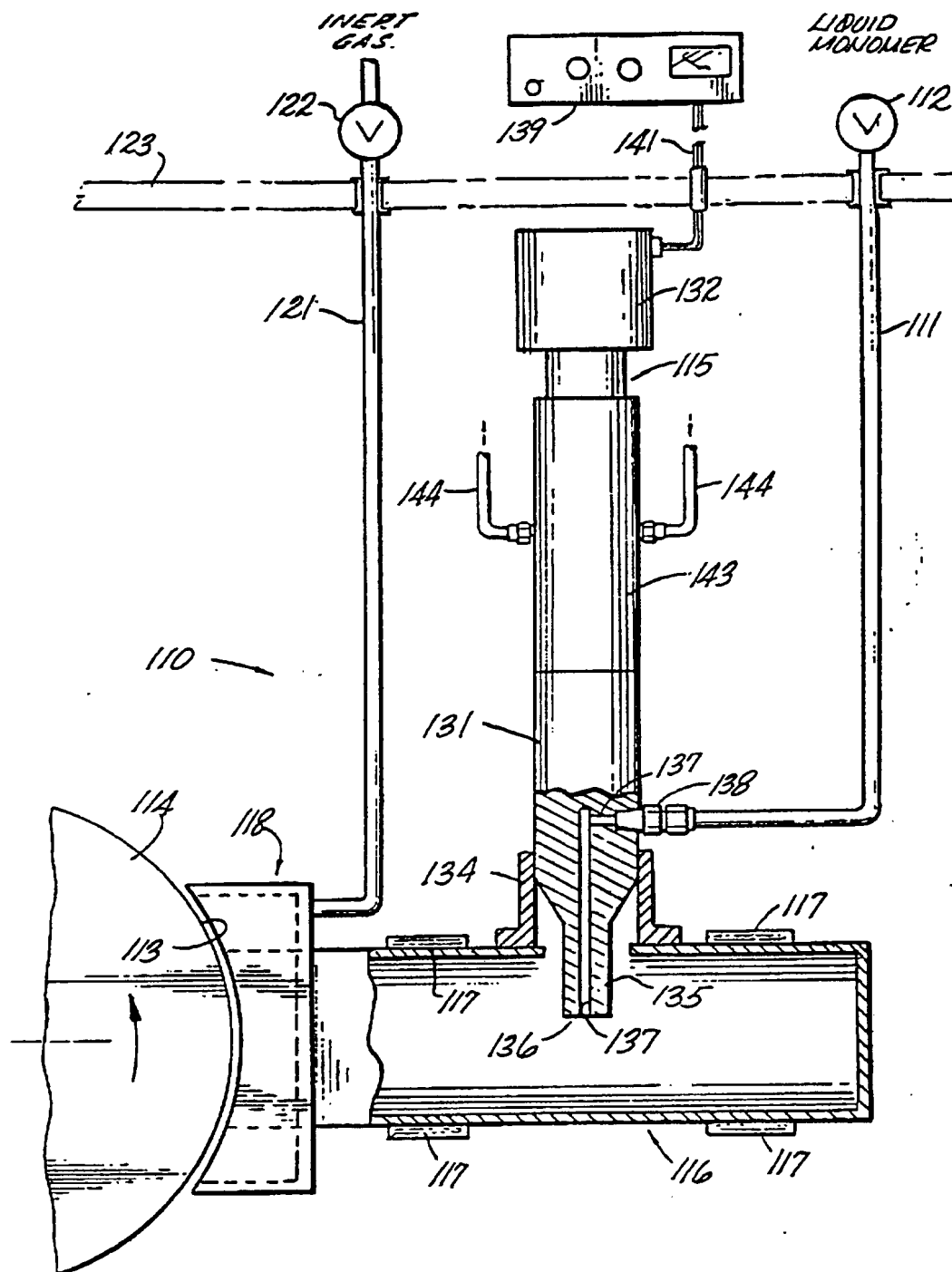
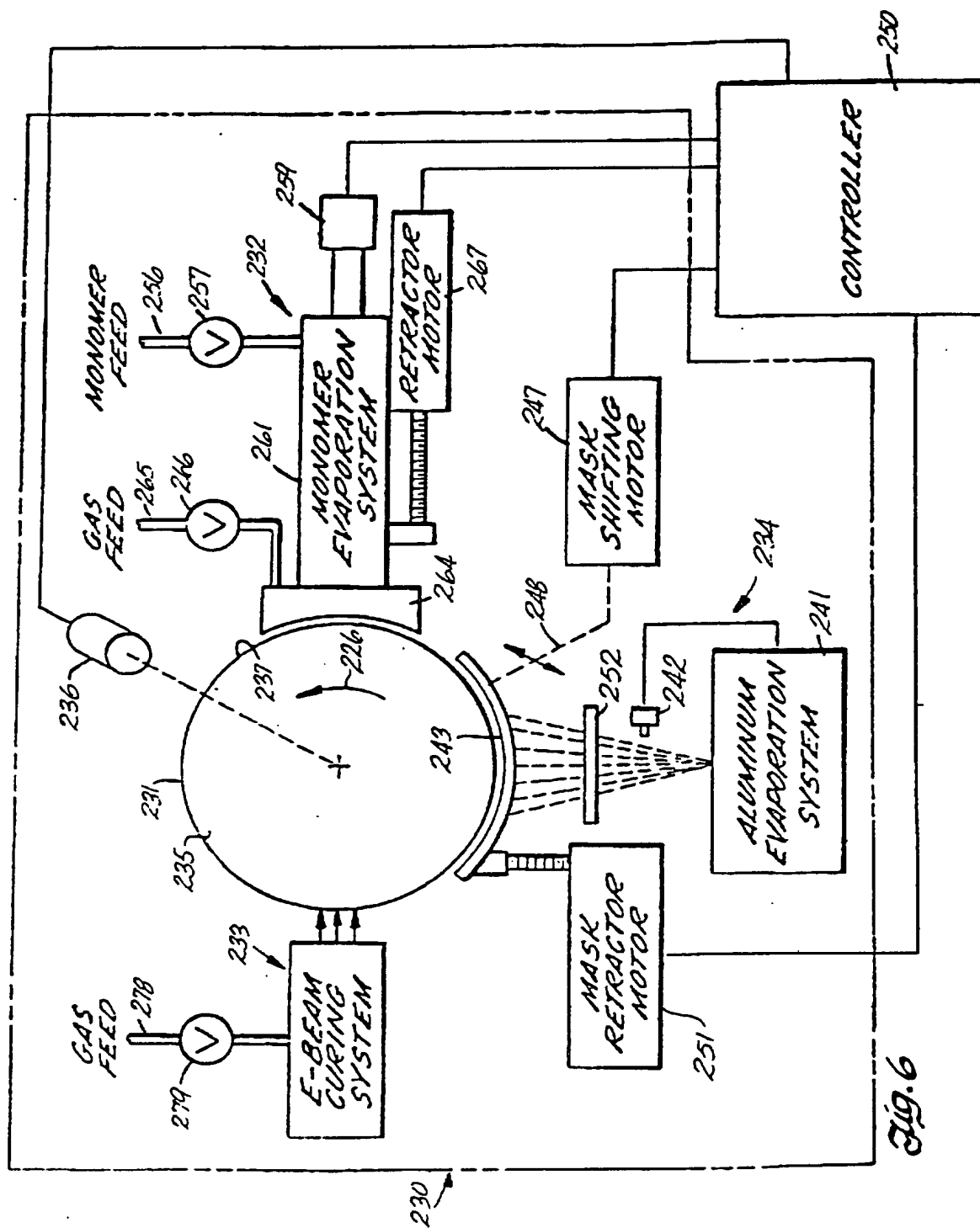


Fig. 5





INTERNATIONAL SEARCH REPORT

International Application No **PCT/US87/01455**

| | | |
|--|--|-------------------------------------|
| I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³ | | |
| According to International Patent Classification (IPC) or to both National Classification and IPC | | |
| IPC ⁴ : B01D 1/16; B05D 1/02, 5/12; C23C16/00 | | |
| US CL 219/273, 275; 427/44, 80, 81, 127, 248.1, 255.6, 421 | | |
| II. FIELDS SEARCHED | | |
| Minimum Documentation Searched ⁴ | | |
| Classification System | Classification Symbols | |
| US | 219/272, 275; 427/44, 255.6 | |
| Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁵ | | |
| III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴ | | |
| Category ⁶ | Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷ | Relevant to Claim No. ¹⁸ |
| Y | US, A, 4,076,866 (PLATAKIS) 28 FEBRUARY 1978, SEE ENTIRE DOCUMENT. | 1-12 |
| Y | US, A, 4,543,275 (AKASHI) 24 SEPTEMBER 1978, SEE ABSTRACT AND COLUMN 2, LINES 59 AND 60. | 1-12 |
| Y | GB, A, 1,253,124 (DAVIES) 10 NOVEMBER 1971, SEE ENTIRE DOCUMENT. | 1-12 |
| Y | JP, A, 59-177365 (MATSUSHITA ELEC. IND KK) 24 MARCH 1983, SEE ABSTRACT. | 1-1.2 |
| <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹³ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div> | | |
| IV. CERTIFICATION | | |
| Date of the Actual Completion of the International Search ¹ | Date of Mailing of this International Search Report ¹ | |
| 06 AUGUST 1987 | 31 AUG 1987 | |
| International Searching Authority ¹ | Signature of Authorized Officer ¹⁹ | |
| ISA/US | J. A. BELL | |

INTERNATIONAL SEARCH REPORT

 Interna: Application No
 PCT/US 96/12288

 A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 B05D7/24 C23C16/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

 Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 B05D C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| A | WO,A,87 07848 (SPECTRUM CONTROL INC) 30 December 1987 see the whole document --- | 1 |
| A | US,A,4 696 719 (BISCHOFF GREGG C) 29 September 1987 see the whole document ----- | 4,5 |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

19 November 1996

Date of mailing of the international search report

28. 11. 96

Name and mailing address of the ISA

 European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax (+31-70) 340-3016

Authorized officer

Brothier, J-A

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | |
|----|------------------------------|----|--|----|--------------------------|
| AT | Austria | FR | France | ML | Mali |
| AU | Australia | GA | Gabon | MR | Mauritania |
| BB | Barbados | GB | United Kingdom | MW | Malawi |
| BE | Belgium | HU | Hungary | NL | Netherlands |
| BG | Bulgaria | IT | Italy | NO | Norway |
| BJ | Benin | JP | Japan | RO | Romania |
| BR | Brazil | KP | Democratic People's Republic of Korea | SD | Sudan |
| CF | Central African Republic | KR | Republic of Korea | SE | Sweden |
| CG | Congo | LI | Liechtenstein | SN | Senegal |
| CH | Switzerland | LK | Sri Lanka | SU | Soviet Union |
| CM | Cameroon | LU | Luxembourg | TD | Chad |
| DE | Germany, Federal Republic of | MC | Monaco | TG | Togo |
| DK | Denmark | MG | Madagascar | US | United States of America |
| FI | Finland | | | | |